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NEW METHOD OF SYNTHESIZING ESTERS OF PHOSPHONOCARBOXYLIC ACIDS AND THEIR DERIVATIVES

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In 1947, while studying the reactions of isomeric methoxychloropentenes with sodium salts of dialkylphosphorous acids, I demonstrated that the alkoxy-dialkylphosphonopentenes which are first formed add, under definite conditions, sodium dialkylphosphite to the double bond to form alkoxy-di-(dialkylphosphono)-pentenes. [1] I later used this interesting observation as a basis for working out a new method of synthesizing esters of phosphonic acids and their various derivatives. This method consists of the addition of dialkylphosphorous, aryl-phosphonous, and alkylphosphonous as well as some sulfur-containing acids of phosphorus to unsaturated electrophilic reagents in the presence of alcoholates of alkali metals.

The proposed new method is very simple and is based on available starting materials. With the aid of this method, various derivatives of phosphonic and thiophosphonic acid esters can be prepared in sufficiently high yields. In our previous work, published in 1950, we described the addition of dialkylphosphorous acids to unsaturated ketones, aldehydes, esters of carboxylic acids, nitriles, and esters of phosphonic acids. [2]

However, reports have recently been published in which the reactions that we investigated and described earlier are repeated by various authors and described as original. Thus, in 1950-51, Rueggeberg, Chernack, and Rose [3] and Schwarzenbach, Rückstuhl, and Zurc [4] described the reaction of sodium diethylphosphite with isomeric allyl halides, and in 1951 Bochwick and Michalski [5] described the addition reaction of dialkyl phosphorous acids and esters of phenylphosphonous acid to esters of unsaturated acids, acronitrile, and benzal acetone.

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Developing the investigations carried out earlier [2], the present work outlines the results of studying the addition reaction of dialkylphosphorous acids and esters of phenylphosphonous acid to unsaturated acids, their amides, esters, and nitriles. The experimental methods were analogous to those described in previous reports [2].

Through the addition of diethyl-n-dipropyl and n-dibutylphosphorous acids to the amide of methacrylic acid, the following amides were obtained: amide of diethylphosphonoisobutyric acid, bp 146-147° at 13 mm, n_D^{20} 1.4361, d_4^{20} 1.0624; amide of n-dipropylphosphonoisobutyric acid, bp 135° at 2 mm, n_D^{20} 1.4438, d_4^{20} 1.0437; and amide of n-dibutylphosphonoisobutyric acid, bp 164-165° at 12 mm, n_D^{20} 1.4421, d_4^{20} 0.9941. The yield of the addition products usually amounted to 25-30%.

By adding the higher dialkylphosphorous acids, i.e., n-diethyl-, n-diheptyl-, and n-dioctylphosphorous acids, to the methyl ester of methacrylic acid, the following methyl esters were prepared: methyl ester of n-diethylphosphonoisobutyric acid, bp 188-189° at 4 mm, n_D^{20} 1.4442, d_4^{20} 0.9600; methyl ester of n-diheptylphosphonoisobutyric acid, bp 183-185° at 1 mm, n_D^{20} 1.4480, d_4^{20} 0.9653; and methyl ester of n-dioctylphosphonoisobutyric acid, bp 193-194° at 1 mm, n_D^{20} 1.4489, d_4^{20} 0.9641.

Through the action of phosphenyl chloride on various alcohols, we next synthesized an entire new series of previously unknown esters of phenylphosphonous acid (up until the present only the butyl ester of phenylphosphonous acid, prepared by G. Kosolapoff [6], was known) and carried out the addition of these esters to methyl methacrylate and some other esters of α , β -unsaturated carboxylic acids.

The following esters of phenylphosphonous acid were obtained with 60-90% yields: methyl, bp 91-93° at 1 mm, n_D^{20} 1.5330, d_4^{20} 1.1770; ethyl, bp 94-95° at 1.5 mm, n_D^{20} 1.5231, d_4^{20} 1.1291; isopropyl, bp 106-107° at 1 mm, n_D^{20} 1.5111, d_4^{20} 1.0922; isobutyl, bp 112-113° at 1 mm, n_D^{20} 1.5081, d_4^{20} 1.0675; n-hexyl, bp 139° at 1 mm, n_D^{20} 1.5030, d_4^{20} 1.0388; n-heptyl, bp 150° at 1 mm, n_D^{20} 1.4996, d_4^{20} 1.0187; n-octyl, bp 155° at 1 mm, n_D^{20} 1.4982, d_4^{20} 1.0079; and n-nonyl, bp 158-160° at 1 mm, n_D^{20} 1.4900, d_4^{20} 0.9643.

By adding the ethyl and isobutyl esters of phenylphosphonous acid to methyl methacrylate, the following were obtained: the ethyl ester of B-(carboxymethyl)-propylphenylphosphonic acid, bp 141-143° at 1.5 mm, n_D^{20} 1.5054, d_4^{20} 1.1390; and the isobutyl ester of B-(carboxymethyl)-propylphenylphosphonic acid, bp 155-156° at 1 mm, n_D^{20} 1.4965, d_4^{20} 1.0662.

By adding the ethyl ester of phenylphosphonous acid to methyl acrylate and to the ethyl ester of cinnamic acid, the following were obtained: the ethyl ester of B-(carboxymethyl)-ethylphenylphosphonic acid, bp 159-160° at 2 mm, n_D^{20} 1.5081, d_4^{20} 1.1619; and the ethyl ester of (α -phenyl- β -carboxymethyl)-ethylphenylphosphonic acid, bp 182° at 1 mm, n_D^{20} 1.5416. The reaction proceeds according to the following scheme $C_6H_5(RO)POH + R'-CH=CH-COOR'' \xrightarrow{RONa} C_6H_5(RO)P(=O)(CH_2CH(R')CH_2COOR'')$, where R, R'', R''' are alkyl groups and R' = H or C_6H_5 .

Saponifying the esters with dilute hydrochloric acid gave the corresponding acids.

We also studied the addition of dialkylphosphorous acids to symmetrical and unsymmetrical dibasic unsaturated acids and their esters.

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The addition of dialkylphosphorous acids to maleic acid takes place very readily; with yields of 60-70%, the following compounds were obtained: Dimethylphosphonosuccinic acid, bp 141° at 3 mm, n_D^{20} 1.4428, d_4^{20} 1.2695; and diethylphosphonosuccinic acid, bp 137-138° at 1 mm, n_D^{20} 1.4408, d_4^{20} 1.1782.

The addition of dialkylphosphorous acids to the esters of maleic and fumaric acids proceeds even more energetically. The dimethyl esters of the following acids were synthesized with 80-95% yields: dimethylphosphonosuccinic acid, bp 142° at 2 mm, n_D^{20} 1.4435, d_4^{20} 1.2076; diethylphosphonosuccinic acid, bp 184° at 13 mm, n_D^{20} 1.4412, d_4^{20} 1.1803; n-dibutylphosphonosuccinic acid, bp 161-162° at 1 mm, n_D^{20} 1.4425, d_4^{20} 1.0666; and the diethyl ester of diethylphosphonosuccinic acid, bp 161-162° at 2 mm, n_D^{20} 1.4410, d_4^{20} 1.1333.

By adding two moles of diethylphosphorous acid to the ethyl ester of acetylidene dicarboxylic acid, the diethyl ester of di-(diethylphosphono)-succinic acid, bp 213-214° at 5 mm, n_D^{20} 1.4700, d_4^{20} 1.3753, was obtained.

The addition of dialkylphosphorous acids to esters of ethylidene- and benzalidene malonic acids takes place just as readily and accompanied by considerable heating of the reaction mixtures.

The ethyl esters of the following acids were synthesized in yields of 70-80% and were found to have the properties listed below: α -(dimethylphosphono)-ethylmalonic acid, bp 181° at 13 mm, n_D^{20} 1.4462, d_4^{20} 1.1748; α -(diethylphosphono)-ethylmalonic acid, bp 180° at 11 mm, n_D^{20} 1.4427, d_4^{20} 1.1172; α -(n-dibutylphosphono)-ethylmalonic acid, bp 203-204° at 11 mm, n_D^{20} 1.4457, d_4^{20} 1.0560; phenyl-(dimethylphosphono)-methylmalonic acid, bp 200-202° at 3 mm, n_D^{20} 1.4975, d_4^{20} 1.2063; phenyl-(diethylphosphono)-methylmalonic acid, bp 212-214° at 11 mm, n_D^{20} 1.4911, d_4^{20} 1.1364; phenyl-(diisobutylphosphono)-methylmalonic acid, bp 219° at 14 mm, n_D^{20} 1.4812, d_4^{20} 1.0475; and phenyl-(n-dibutylphosphono)-methylmalonic acid, bp 218-220° at 11 mm, n_D^{20} 1.4820.

With somewhat lower yields (65-70%), the addition products of dialkylphosphorous acids to ethylidene- and benzalidene-acetic acid were obtained, i.e., the ethyl esters of α -(dimethylphosphono)-ethylacetoacetic acid, bp 164-167° at 14 mm, n_D^{20} 1.4703, d_4^{20} 1.1473; phenyl-(dimethylphosphono)-methylacetoacetic acid, bp 193-195° at 6 mm, n_D^{20} 1.5295, d_4^{20} 1.2096; phenyl-(diethylphosphono)-methylacetoacetic acid, bp 204-206° at 7 mm, n_D^{20} 1.5195, d_4^{20} 1.1836; phenyl-(diisobutylphosphono)-methylacetoacetic acid, bp 204-205° at 6 mm, n_D^{20} 1.4970, d_4^{20} 1.1104; and phenyl-(n-dibutylphosphono)-methylacetoacetic acid, bp 195-197° at 15 mm, n_D^{20} 1.4808, d_4^{20} 1.0441.

In conclusion, we studied the addition of dialkylphosphorous acids to nitriles of the following unsaturated acids: methacrylic, vinylacetic, crotonic, pyromucic, and cyclohexenecarboxylic.

In one of the previous investigations, it was demonstrated that the lower dialkylphosphorous acids add to the nitrile of acrylic acid very energetically with the formation of the corresponding esters of β -cyanopropylphosphonic acid [2]. In the present work, we demonstrate the possibility of adding also higher dialkylphosphorous acids, i.e., diisooamyl-, dihexyl-, and n-dioctylphosphorous acids, to acronitrile.

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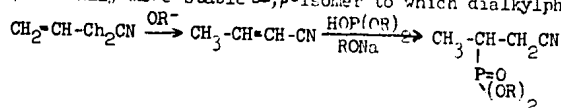
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The nitriles of the following acids were obtained with 60-65% yields and their properties found to be as follows: β -(diisocamylphosphono)-propionic acid, bp 168-170° at 3 mm, n_D^{20} 1.4467, d_4^{20} 1.0190; β -(n-diethylphosphono)-propionic acid, bp 198-200° at 1 mm, n_D^{20} 1.4462, d_4^{20} 0.9963; and β -(n-diethylphosphono)-propionic acid 218-220° at 2 mm, n_D^{20} 1.4495, d_4^{20} 0.9676.

By adding dialkylphosphorous acids to the nitrile of methacrylic acid, the following were obtained with 60-65% yields: the dimethyl ester of β -cyanopropylphosphonic acid, bp 141-142° at 11 mm, n_D^{20} 1.1502, d_4^{20} 1.4351; the diethyl ester of β -cyanopropylphosphonic acid, bp 146-147° at 11 mm, n_D^{20} 1.4364, d_4^{20} 1.0943; and the n-dibutyl ester of β -cyanopropylphosphonic acid, bp 180-182° at 12 mm, n_D^{20} 1.4401, d_4^{20} 1.0103.

By adding dialkylphosphorous acids to the nitriles of vinylacetic and crotonic acids, addition products were obtained that were identical according to their constants, i.e., the nitriles of β -methyl- β -(dimethylphosphono)-propionic acid, bp 143-144° at 10 mm, n_D^{20} 1.4431, d_4^{20} 1.1596; β -methyl- β -(diethylphosphono)-propionic acid, bp 149-150° at 12 mm, n_D^{20} 1.4370, d_4^{20} 1.0824; and β -methyl- β -(n-dibutylphosphono)-propionic acid, bp 176-178° at 12 mm, n_D^{20} 1.4445, d_4^{20} 1.0186.

Apparently, when there are alkoxy anions present, there takes place in the reaction process a prototropic isomerization of the β,γ -unsaturated nitrile into the thermodynamically more stable α,β -isomer to which dialkylphosphorous acids then add:



As a result of the reaction between the nitrile of pyromucic acid and diethylphosphorous acid, the diethyl ester of α -cyano- β -dihydrofuran-2-carboxylic acid, bp 130-133° at 6 mm, n_D^{20} 1.4873, d_4^{20} 1.1919, was obtained. When heated, the addition product readily decomposes into its original components. This process takes place even more readily in the case of the addition product of dialkylphosphorous acids to cyancyclohexene, which could not be separated in the pure form.

D. A. Yarmukhametov and N. I. Plakatina collaborated in the work reported in this paper.

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